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PHOTODETACHMENT STUDIES OF
MOLECULAR NEGATIVE IONS

Final Report

E. C. Beaty and W. C. Lineberger

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A drift tube mass spectrometer and an ion beam machine have been used with a flashlamp pumped tunable dye laser to study photodestruction of atmospheric molecular negative ions. Results are presented for O_2^- , O_3^- , CO_3^- , and NO_2^- . Problems inherent with the technique and possible improvements are discussed.		

I. INTRODUCTION

The work reported here consists of two phases: 1) a measurement of photodetachment and photodissociation cross sections for thermalized molecular negative ions using a drift tube mass spectrometer, and 2) studies of photodetachment of molecular negative ions in a crossed beam machine in wavelength regions not accessible to the drift tube techniques. The overall objective is to provide some of the information required to predict the effect of light on a decaying atmospheric plasma. Negative ions play an important role in controlling the electrical conductivity of the atmosphere. Free electrons attach to neutral molecules to form negative ions, removing the electrons as effective conductors. Through the mechanism of photodetachment, a distant source can remove the electrons from the negative ions and significantly increase the atmospheric conductivity. The photodissociation process changes the identity of the negative ion and hence, given the spectral range of the incident light, may either increase or decrease the net photodetachment rate. In the earth's atmosphere a chain of reactions leads to negative ions which have relatively long lifetimes and which are destroyed either by ion-ion recombination or by photons. These ions are generally called "terminal" ions. In order to predict the densities of these terminal negative ions, it is necessary to account quantitatively for the effect of photodestruction, including knowledge of both photodetachment and photodissociation cross sections for these ions extending into the ultraviolet. In the lower D-region, the dominant terminal ions are presently considered¹ to be NO_2^- , NO_3^- , CO_3^- , CO_4^- , and hydrates of these. In addition to knowledge of the photodestruction of these species it is clearly important to have information on changes in electron binding energies as clustering proceeds. In the following sections we report on our progress during the

period of this grant, and indicate briefly some of the problems remaining to be solved.

II. RESEARCH PROGRAM

Experimentally, molecular negative ions present very different problems from atomic negative ions. The reason is of course that atomic negative ions have few if any excited states. This paucity of excited states has meant that hot ion source beam techniques provide no substantial difficulty² in the interpretation of atomic negative ion photodetachment data. On the other hand, the plethora of vibrational and rotational states of molecular negative ions which are excited in hot ion sources can make it very difficult to interpret molecular ion photodetachment data, except in favorable circumstances. While we have been able to interpret such data for several ions,^{3,4} it is distinctly preferable to study vibrationally relaxed ions such as are produced in a drift tube source. The principal drawback of such a source has been the low intensity negative ion beam (or swarm) so produced, and the resulting lower signal-to-noise ratio which (using current laser sources) has restricted the wavelength region accessible to the red half of the visible spectrum. In the remainder of this section we will discuss the drift tube photodetachment results, the beam photodetachment results and future developments.

A. Drift Tube Studies

For some years Beaty and coworkers have been studying photodetachment of molecular ions in a drift tube. In these measurements, the vibrational excitation problem was solved by keeping the ions at relatively high pressure. Photodetachment information was obtained^{5,6} for O_2^- and O_3^- . However a

mass spectrometer was not incorporated in this apparatus, and it was necessary to use ion mobility to distinguish the ions. For the terminal negative ions, a mobility determination is not adequate and modifications were made to permit the use of a mass spectrometer with this photodetachment apparatus. Such a modification was completed, and a flashlamp pumped, pulsed tunable dye laser was used as the light source.

The principal problem with such an experimental arrangement is that signal levels are rather low, and, in order to obtain a reasonable data rate, it is necessary to use a light source with a much higher average power than is obtainable from the pulsed dye laser. In spite of these difficulties it was possible to study the photodestruction of CO_3^- , and to show⁷ that the dominant loss mechanism in the photon energy range 1.75-2.15 eV was photodissociation to produce O^- . The observed photodissociation cross section was highly structured; this structure has been confirmed and the studies greatly extended in the very beautiful experiments^{8,9} of Moseley and coworkers at Stanford Research Institute. The SRI experiments have much greater resolution and data gathering ability, largely as a result of the much higher average power (4000 times higher) obtainable from a continuous dye laser excitation source. We plan no further experiments of this type.

B. Tunable Laser Crossed Beam Experiments

The basic crossed tunable laser-ion beam machine has been successfully used for several years in studies of atomic negative ion photodetachment, and the details of the technique can be found elsewhere.¹⁰ Basically a several kilovolt mass analyzed beam of negative ions is crossed with the output of a pulsed tunable dye laser, and the photodetachment products are analyzed as a function of photon energy. Early experiments detected only

the neutral products and hence for molecular negative ions produced a photodestruction cross section, for which one must use separate physics to decide whether the destruction process is photodetachment, photodissociation or both.

The apparatus was utilized to study photodetachment of NO_2^- in the photon energy range 1.8-2.7 eV. The details of this measurement⁴ are contained in a reprint included as Appendix A. As a result of the fact that the geometry of NO_2^- and NO_2 are quite different, a detailed Franck-Condon factor analysis was required to deduce the electron affinity. Completion of this analysis allows prediction of the NO_2^- photodetachment cross section at D-region temperatures.

In addition to the normal NO_2^- , we observe photodetachment of another form of NO_2^- with an apparent threshold near 1.8 eV. There are three reasonable choices for the identity of this ion: 1) a highly excited set of vibrational levels of $X^1A_1 \text{NO}_2^-$; 2) an excited metastable triplet state of NO_2^- ; 3) a peroxy isomer of NO_2^- . We present plausibility arguments which suggest that the most reasonable choice is the third. Recently, Moseley¹¹ has shown that similar results can be obtained in the photon energy region 2.0-2.3 eV under conditions such that the excitation of the ion is undoubtedly vibrational. The observation does not rule out the possibility of a peroxy isomer, but reinforces the conclusion that the photoelectron spectra^{12,13} of NO_2^- should be investigated to resolve unequivocally this issue.

III. CONCLUSIONS AND RECOMMENDATIONS

The studies described above demonstrate clearly the desirability of producing a beam or swarm of vibrationally relaxed negative ions prior to the photon interaction. Current ion source intensity limitations, however,

require the use of very high average power light sources to study vibrationally relaxed ions. Such sources are currently available only in the range 5000-7000 Å. The beam techniques, on the other hand, have sufficient sensitivity to utilize light sources out to approximately 2600 Å, but in order to obtain sufficient beam currents, one must give up the vibrationally relaxed ions. Several possibilities exist for remedying these problems.

It appears feasible to design negative beam sources which are moderately intense and significantly cooler vibrationally than current ones. The rapid development of the rare gas halide excimer lasers indicates that their use as a pumping source for tunable dye lasers in the blue and near ultraviolet may greatly increase the average power available for a photodetachment experiment. Using such a light source together with the somewhat cooler negative ion beams should produce a significant increase in both the quantity and quality of near ultraviolet photodestruction cross section measurements.

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Laser photodetachment of NO_2^- *

E. Herbst, T. A. Patterson, and W. C. Lineberger†

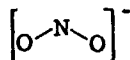
Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards, and Departments of Chemistry and Physics and Astrophysics, University of Colorado, Boulder, Colorado 80302

(Received 18 March 1974)

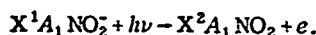
An absolute apparent cross section for the photodetachment of nitrite (NO_2^-) ions has been measured in the region (2.0–2.7) eV utilizing a tunable dye laser as the light source. The electron affinity of nitrogen dioxide (NO_2) has been determined to be (2.36 ± 0.10) eV. Photodetachment of an ion thought to be a peroxy isomer of NO_2^- has also been observed.

I. INTRODUCTION

The tunable laser photodetachment method has been very productive in determining electron affinities and photodetachment cross sections for a variety of atomic species.^{1,2} Recently, the method has been utilized to study the diatomic ion OH^- .³ This paper reports a tunable laser photodetachment study of the nitrite ion (labelled NO_2^-) of molecular geometry

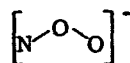


The particular process studied is



The dependence on photon energy of the absolute (ion temperature-dependent) apparent cross section is measured in the vicinity of the NO_2^- photodetachment onset (2.0–2.65) eV at an ion temperature $T \approx 1500$ – 2000 °K. By theoretical reproduction of the observed spectrum, we are able to deduce a value of (2.36 ± 0.10) eV for the electron affinity of nitrogen dioxide (NO_2). The apparent cross section for NO_2^- photodetachment is a strong function of ion temperature in the energy region studied. Our analysis permits estimation of this quantity at other temperatures, including specifically temperatures that pertain in the atmospheric D region.

In addition to NO_2^- , photodetachment of another ion of $m/e = 46$ is observed. This unusual ion, labelled NO_2^{*-} , is probably a peroxy isomer of NO_2^- ,⁴ of molecular geometry



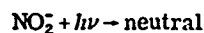
II. EXPERIMENTAL

The apparatus and data analysis used in this work have been fully described previously.¹ A 2.5 keV beam of negative ions is extracted from a hot cathode plasma ion source at estimated temperature $T \approx 1500$ – 2000 °K, mass analyzed as $m/e = 46$, and intersected by radiation from a pulsed flashlamp-pumped, tunable dye laser of ~ 1 Å bandwidth. Ion currents, typically ≥ 100 nA, are detected on a Faraday cup. Photodetached neutrals strike the cathode of a multiplier and are detected by the resultant electron current. Analysis of the data yields an apparent cross section (σ'_{app}) as a function of photon energy E given by the formula

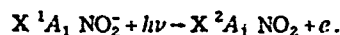
$$\sigma'_{\text{app}}(E) = \sum_{k=1}^{200} \frac{[NS(k) - NB(k)] - LEN}{[IS(k)][LS(k)]}, \quad (1)$$

where k represents the k th laser firing ($1 \leq k \leq 200$) at a given frequency, $NS(k)$ is the neutral signal (photodetached and charge-stripped on the background gas) on the k th firing, $NB(k)$ is the neutral signal (charge-stripped) just prior to the k th firing, $IS(k)$ is the ion beam current during the k th firing, $LS(k)$ is the laser flux at the k th firing, and LEN is the laser electrical noise induced in the neutral detector. The measured relative cross section σ'_{app} , accurate to $\pm 10\%$, is in general the sum of cross sections for photodetachment and photodissociation. An absolute apparent cross section (labelled σ_{app}) is obtained by comparison with the known absolute cross section for O^- photodetachment.^{1,5} Corrections must be made for the difference in multiplier gain between O atoms and the particular neutrals being formed (e.g., NO_2) as well as for the different velocities of iso-energetic O^- and NO_2^- ions which result in different times spent in the intersection with the laser beam.

In this experiment, ions are produced in the plasma source from two neutral gaseous precursors. The first gas utilized is O_2 and a trace of N_2 . Photon bombardment of the ion beam at $m/e = 46$ reveals two distinct ionic species, one of which produces neutrals when intersected with photons of energy ≥ 1.8 eV while the other requires photons of energy ≥ 2.2 eV. Variation of the source parameters allows good selection of one ion or the other. Nitrogen dioxide, the other gas used, forms only that ion which produces neutrals upon interaction with photons of energy ≥ 2.2 eV. This ion must clearly be NO_2^- because the electron affinity of NO_2 has been measured by a variety of techniques to be (2.4 ± 0.2) eV.⁶⁻⁸ The process measured



is undoubtedly completely photodetachment since the lowest energy photodissociation channel does not open until ≈ 4 eV. The photodetachment process involves the ground electronic states of both NO_2^- and NO_2 :



The other ion, labelled NO_2^{*-} , is thought to be a peroxy isomer of NO_2^- (see Sec. V). Upon interaction with photons of energy ≥ 1.8 eV, it photodetaches via the probable mechanism



The absolute cross sections (σ_{app}) for NO_2^- and NO_2^{*-} photodetachment determined by the approach outlined above are presented in Fig. 1. The absolute cross sec-

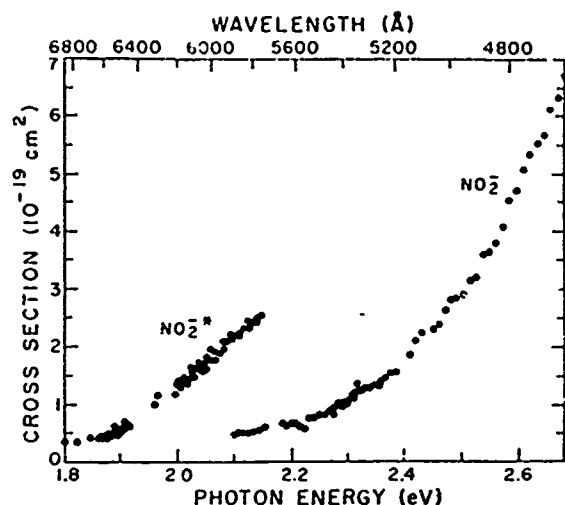
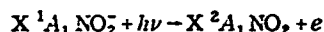


FIG. 1. Apparent cross sections for photodetachment of NO₂* and NO₂ in the region (1.8–2.7) eV. Although the relative cross sectional values have been measured to an accuracy of 10%, the absolute values are known only to $\pm 40\%$.

tion scale shown is accurate to $\pm 40\%$ for NO₂*. When the O₂ source is utilized, it is unclear whether variation of the source parameters allows total selection of NO₂* or NO₂*. If the NO₂* beam contains a small percentage of NO₂, the σ_{app} for NO₂* photodetachment determined by our approach is too low because NO₂ has a much smaller cross section for photodetachment than does NO₂* at the energies involved (1.8–2.2 eV). [See Expression (1).] Thus, within the $\pm 40\%$ error bounds, the absolute NO₂* cross section shown in Fig. 1 is a lower bound to the true cross section. The data labelled NO₂ in Fig. 1 are obtained using NO₂ as the gas in the ion source.

III. SIMULATION OF NO₂ PHOTODETACHMENT SPECTRUM

The photodetachment process



consists of numerous transitions from vibrational states i of 1A_1 NO₂ to such states j of 2A_1 NO₂.⁹ Each of these transitions has a cross-sectional dependence on energy in the threshold region that is not well understood. For a $p\pi$ electron departing a molecule with a permanent dipole moment, this dependence is probably between a step function and a square root function.³ In this work it is assumed that¹⁰

$$\sigma_{ij}(E - E_{ij}) = \sigma^0 |I_{ij}|^2 (E - E_{ij})^{1/4}, \quad (2)$$

where σ_{ij} is the cross section for the $i \rightarrow j$ channel with threshold energy E_{ij} (cm⁻¹), $E \geq E_{ij}$ is the photon energy, I_{ij} the vibrational overlap integral between states i and j , and σ^0 a multiplicative factor. The threshold energy is given by the expression

$$E_{ij} = EA(\text{NO}_2) + E_j - E_i, \quad (3)$$

where E_j , E_i are the energies of states j , i relative to the ground vibrational levels of the respective electronic states and $EA(\text{NO}_2)$, the NO₂ electron affinity, is defined

as the energy separation between the ground vibrational levels. The apparent total cross section, which is the quantity measured in this experiment, can be obtained from the expression

$$\sigma_{app}(E) = \sum_{i,j} \sigma_{ij}(E - E_{ij}) N_i / \sum_i N_i, \quad (4)$$

where N_i is the density of NO₂* molecules in state i . If the NO₂* vibrational distribution is assumed to be Boltzmann, then the factor $N_i / \sum_i N_i$ reduces to a Boltzmann factor. The summation over j levels in expression (4) is restricted to those channels for which $E_{ij} \leq E$.

The calculation of Franck-Condon factors (I_{ij})¹² is necessary to obtain σ_{app} . Both 1A_1 NO₂* and 2A_1 NO₂ are nonlinear molecules of symmetry C_{2v} and possess three normal modes of vibration— $\nu_1(A_1)$, $\nu_2(A_1)$, $\nu_3(B_2)$ —labelled the symmetric stretch, bend, and asymmetric stretch respectively.¹¹ Table I lists the frequency of these modes as well as additional information concerning the ground electronic states of NO₂* and NO₂. The NO₂* vibrational data are gathered from condensed phase studies of nitrite ions in interactive environments and are only approximately correct for the free gas phase species. A recent infrared study of NO₂* in a noninteracting argon matrix has yielded an asymmetric stretching frequency of 1244 cm⁻¹ which is in good agreement with the value used in this work.¹²

The overlap integral I is given by the formula

$$I(\nu'_1 \nu'_2 \nu'_3 - \nu_1 \nu_2 \nu_3) = \int \int \int \psi_{\nu'_1 \nu'_2 \nu'_3}^* (Q'_1 Q'_2 Q'_3) (\psi_{\nu_1 \nu_2 \nu_3} (Q_1 Q_2 Q_3)) dQ_1 dQ_2 dQ_3. \quad (5)$$

Unprimed variables represent NO₂* whereas primed variables represent NO₂. The vibrational wavefunctions are functions of the normal coordinates Q_i , Q'_i ($i=1, 2, 3$) with quantum numbers ν_i , ν'_i ($i=1, 2, 3$) and, in the harmonic approximation, are products of one-dimensional harmonic oscillator functions.¹¹ The integral is arbitrarily taken over NO₂* coordinates. To integrate (5), it is necessary to express the NO₂ normal coordinates Q' in terms of the NO₂* coordinates Q :

TABLE I. Parameters of NO₂(¹A₁) and NO₂(²A₁).

	NO ₂ *	NO ₂
ν_1 (cm ⁻¹)	1332 ^a	1320 ^b
ν_2 (cm ⁻¹)	921 ^a	750 ^b
ν_3 (cm ⁻¹)	1240 ^a	1617.75 ^b
$d(\text{N-O})$ (Å)	1.236 ^c	1.1934 ^d
α (<O-N-O)	115.4 ^c	134.1 ^d
f_{11} (mdyn/Å)	9.85 ^a	12.43 ^b
f_{22}/d^2 (mdyn/Å)	1.7 ^a	1.096 ^b
f_{33}/d (mdyn/Å)	0.505 ^a	0.535 ^b

^aThese are averaged from NaNO₂ (aqueous) data. See R. E. Weston, Jr. and T. F. Brodasky, J. Chem. Phys. 27, 683 (1957).

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TABLE II. Calculated Franck-Condon factors for the transition^a $h\nu + X^1A_1NO_2(0, v_2, 0) \rightarrow X^2A_1NO_2(0, v_2', 0) + e$.

v_2'	0	1	2	3	4	5	6
0	0.0026	0.0119	0.0115	0.0171	0.1077	0.1139	0.1162
1	0.0088	0.0322	0.0133	0.0343	0.0961	0.0433	0.0217
2	0.0121	0.0229	0.0098	0.0093	0.0136	0.290	0.0000
3	0.0179	0.0114	0.0008	0.0127	0.0298	0.018	0.02
4	0.0100	0.0001	0.0007	0.0000	0.0000	0.115	0.0432
5	0.0016	0.0000	0.0072	0.0000	0.0000	0.113	0.0009
6	0.0007	0.0000	0.0013	0.0000	0.0770	0.116	0.0187

^aHarmonic approximation.

$$Q' = JQ - K \quad (6)$$

It can be shown that the orthogonal matrix J connects only those normal modes of the same symmetry and that K has nonzero elements only for totally symmetric (A_1) modes.^{13,14} As a result, Eq. (5) simplifies to

$$H(r_1' r_2' r_3' - r_1 r_2 r_3) = \int \int \psi_{r_1}^*(Q_1') \psi_{r_2}^*(Q_2') \psi_{r_3}^*(Q_3) \psi_{r_1}(Q_1) \psi_{r_2}(Q_2) dQ_1 dQ_2 \times \int \psi_{r_3}^*(Q_3) \psi_{r_3}(Q_3) dQ_3. \quad (7)$$

The single integral in the $Q_3(B_2)$ coordinate is easily ascertained. For a mode of symmetry other than A_1 , the only nonzero overlap integrals are those involving transitions of zero or an even number of quanta.¹⁵ Use of Ansacker's¹⁶ analytical expression for the harmonic oscillator overlap integral reveals that in this instance $\Delta r_3 = \pm 2, \pm 4, \dots$ transitions have less than 1% of the intensity of diagonal transitions and are ignored. The four $r_3' - r_3$ transitions considered are 0-0, 1-1, 2-2, 3-3; their overlap integrals are nearly unity.

Evaluation of the double integral in (5) involving the two A_1 coordinates requires a knowledge of J and K . The prerequisite matrix elements are obtained by standard solutions of the vibrational eigenvalue problem to yield^{11,13,14}

$$\begin{aligned} Q_1' &\approx 0.95 Q_1 - 0.31 Q_2 + 2.08 \times 10^{-21} (g^{1/2} - \text{cm}) \\ Q_2' &\approx 0.31 Q_1 + 0.95 Q_2 + 8.55 \times 10^{-21}. \end{aligned} \quad (8)$$

Since the O-N-O angle in NO_2 is $\approx 19^\circ$ larger than in NO_2^- (Table I), it is expected that overlap integrals involving the bending mode will be quite off-diagonal. The N-O internuclear distance does not vary greatly from NO_2^- to NO_2 , but the symmetric stretch normal mode has a sufficient amount of "bend" so that overlap integrals involving this coordinate are also expected to be somewhat off-diagonal. The double integral is computed numerically for 49 bending transitions involving the levels $0 \leq v_2 \leq 6$ and $0 \leq v_2' \leq 6$ for the symmetric stretch transitions ($v_1' - v_1$): 0, 1, 2-0; 0, 1, 2, 3-1; 0, 1, 2, 3, 4-2; 0, 1, 2, 3-3.

We are now able to compute the Franck-Condon factors for most of the transitions occurring in the vicinity ($\pm 3000 \text{ cm}^{-1}$) of the NO_2^- photodetachment onset [$E \sim EA(NO_2^-)$] and originating from vibrational levels within 4500 cm^{-1} of the ground NO_2^- level. As examples, the Franck-Condon factors for the transitions $0v_2'0 - 0v_20$ are listed in Table II.

To simulate the experimental photodetachment spectrum, it is necessary to estimate the source temperature T . One then varies the unknown parameters— σ^0 and $EA(NO_2^-)$ —until a satisfactory fit is obtained between the calculated curve of σ_{app} vs E , determined by expressions (2)–(4), and the experimental spectrum. The estimated source vibrational temperature is in the range $1500 \text{ K} \leq T \leq 2000 \text{ K}$. Figure 2 depicts the best fit to the experimental data at 1500 K . By varying such parameters as the ion "temperature," and the form of the threshold law, we arrive at the conclusion

$$EA(NO_2^-) = (2.36 \pm 0.10) \text{ eV}.$$

The principal source of error in this determination lies in the applicability of the model. If both the threshold law and a true ion temperature were known, then we could obtain a fit accurate to $\pm 0.01 \text{ eV}$. In fact we must vary the NO_2^- vibrational distribution and the threshold law to determine the sensitivity of $EA(NO_2^-)$ to variations in these essentially unknown quantities. It is these variations which give rise to the quoted $\pm 0.10 \text{ eV}$ uncertainty. Thus changing the threshold law from E^3 to $E^{1/2}$ gives rise to a $\pm 0.05 \text{ eV}$ uncertainty, although neither of these limiting cases is expected, and the quality of the fit obtained is poorer than in the case of the $E^{1/4}$ law actually adopted. Other such contributions include correlation with the scale parameter $\sigma^0 (\pm 0.03 \text{ eV})$, uncertainty in the ion source "temperature" ($\pm 0.03 \text{ eV}$), and neglect of rotational effects ($\pm 0.01 \text{ eV}$). Our reported error of $\pm 0.10 \text{ eV}$ for $EA(NO_2^-)$ is our best estimate of the combined effects of these several error sources.

The NO_2^- photodetachment cross section is of interest in D -region chemistry. Utilizing values of σ^0 and $EA(NO_2^-)$ obtained from a fit to the data at $T = 1750 \text{ K}$, we are able to estimate σ_{app} vs E in the onset region [$E \sim EA(NO_2^-)$] at $T = 250 \text{ K}$, a relevant atmospheric temperature. This is shown in Fig. 3. It should be noted that σ_{app} is a strong function of temperature only in the vicinity of $E \sim EA(NO_2^-)$ where relatively few channels are open among accessible levels of NO_2^- .

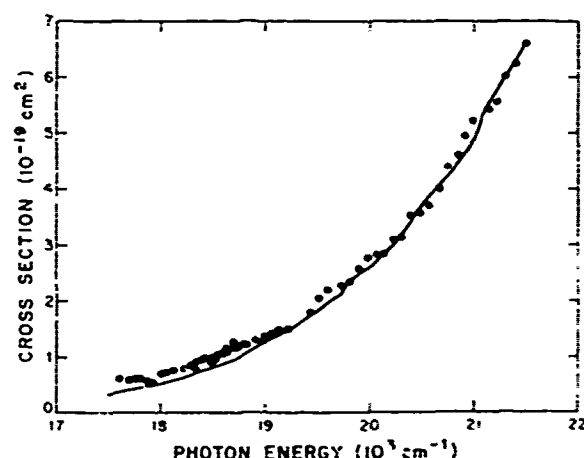


FIG. 2. Observed and simulated apparent cross sections for NO_2^- photodetachment in the region $17.500\text{--}21.500 \text{ cm}^{-1}$ (2.17–2.67 eV). The points represent experimentally determined values while the line represents the best fit to the data at $T = 1500 \text{ K}$.

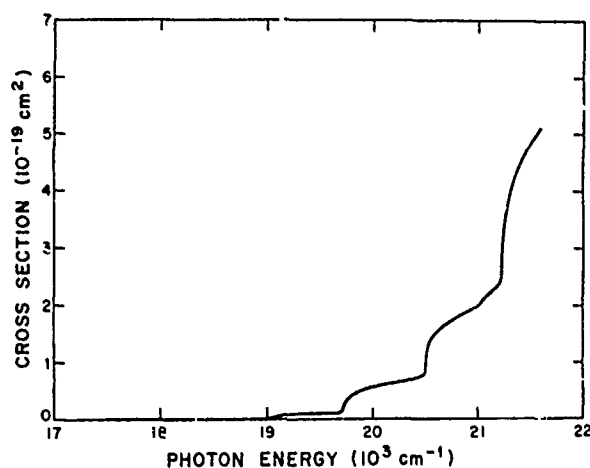


FIG. 3. Calculated apparent cross section for NO_2^- photodetachment in the region 17 500–21 500 cm^{-1} (2.17–2.67) eV at $T = 250^\circ\text{K}$. Rotational effects, which would broaden the sharp discontinuities in the curves, are not included.

IV. DISCUSSION OF NO_2 ELECTRON AFFINITY

The NO_2 electron affinity determined by tunable laser photodetachment is at least 0.4 eV lower than the lowest affinity determined by photodetachment studies using conventional light sources.^{4,17} The reason for this difference is that the Franck-Condon factors for the photodetachment transition are quite off diagonal. [The transition $\text{NO}_2^-(0, 0, 0) \rightarrow \text{NO}_2(0, 0, 0)$ has a Franck-Condon factor of 0.003.] The advantage of laser photodetachment in this case lies in the intensity of radiation available in a narrow bandwidth which permits measurement of absolute cross sections as small as $2\text{--}3 \times 10^{-20} \text{ cm}^2$.

The electron affinity reported here is in excellent agreement with charge-transfer studies. Dunkin *et al.*⁶ report a value of (2.36 ± 0.06) eV whereas Hughes *et al.*⁷ report a value of (2.28 ± 0.10) eV. Charge transfer studies rely, however, on knowledge of the electron affinities of other species while laser photodetachment has no such handicap.

To confirm the reliability of our theoretical analysis, we have examined the recent NO_2^- photodetachment study of Richardson *et al.*⁴ These authors produced NO_2^- at room temperature in an ion cyclotron apparatus and photodetached the ion with conventional light sources of bandwidth ± 0.2 and ± 0.4 eV. If we utilize our calculated σ_{app} vs E curve at $T = 250^\circ\text{K}$ (Fig. 3) and convolute σ_{app} with an appropriate spectral resolution function, we are able to reproduce approximately the long wavelength edge of the NO_2^- photodetachment spectrum of Richardson *et al.*⁴

The tunable laser photodetachment method can be utilized to determine the affinities of a wide variety of molecules provided that there is some knowledge of the valence force constants of both the neutral species and the negative ion. Otherwise, fixed frequency laser photoelectron spectroscopy may be preferable.¹⁸

V. NO_2^*

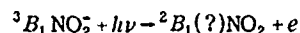
The unusual ion of $m/e = 46$ produced in our plasma source by electron bombardment of O_2 (in the presence of trace amounts of N_2) has been designated NO_2^* . There are three reasonable choices for the identity of NO_2^* :

- (1) a highly excited set of vibrational levels of $X^1A_1 \text{NO}_2^-$;
- (2) an excited metastable triplet state of NO_2^- ;
- (3) a peroxy isomer of NO_2^- .

By the third possibility, we mean specifically that the potential surface for the ground state of NO_2^- has a second minimum at internuclear distances quite distinct from those of ordinary NO_2^- .

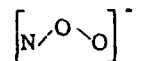
The possibility that NO_2^* is vibrationally excited $^1A_1 \text{NO}_2^-$ is a remote one. If the plasma source is roughly in thermal equilibrium vibrationally, our Franck-Condon analysis predicts a minimum temperature of 5000 K necessary to simulate the onset of the NO_2^* photodetachment spectrum. It is unreasonable to assume that the minor change in source parameters which results in NO_2^* production rather than NO_2^- production can triple the estimated vibrational temperature. There is no previous evidence for such a high vibrational temperature.

The lowest reported triplet state of NO_2^- , of 3B_1 symmetry, has its ground vibrational level 18 959 cm^{-1} above the 1A_1 state.¹⁹ This level lies less than 100 cm^{-1} below the ground state of NO_2 and is the only vibrational level of the 3B_1 state stable with respect to "autodetachment" into $\text{NO}_2 + e^-$.²⁰ The onset of the process¹⁵

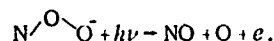


occurs at ≤ 1.9 eV in agreement with the observed NO_2^* photodetachment onset. It is difficult, however, to imagine efficient production of such a fragile and highly energetic metastable in our source. An additional argument against possibilities (1) and (2) is the observation by Richardson *et al.*⁴ of an anomalous form of NO_2^- existing in an ion cyclotron trap on the order of seconds.

We are left with the third possibility; namely, that NO_2^* is a peroxy isomer of NO_2^- of probable electronic structure



This possibility is strengthened by the existence of the isoelectronic N-O-F .²¹ Previous investigators^{4,22} have reported evidence for a peroxy form of NO_2^- . In addition, strong evidence exists for a peroxy form of the ion NO_3^- (O-O-N-O^-).²³ Let us assume that the oxygen-oxygen bond in NO_2^* is a weak electrostatic interaction between NO and O^- . Then, the photodetachment process is probably

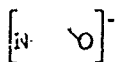


An approximate onset for this process can be obtained from the expression

$$E_{\text{onset}} \approx EA(\text{O}) + \bar{E}(T),$$

where \bar{E} is the average bond energy between NO and O^-

at temperature T . If the NO \cdots O \cdots bond were partly electrostatic, a reasonable estimate for $\bar{I}(T \approx 1500 \text{ K})$ would be $\approx 0.5 \text{ eV}$.²⁴ Then, since $EA(\text{O}) = 1.46 \text{ eV}$,²⁵ $E_{\text{onset}} \approx (1.9 - 2.0) \text{ eV}$, in reasonable agreement with observation (Fig. 1). To prove the existence of



more rigorously, a laser photoelectron study should be undertaken.¹⁶

VI. SUMMARY

We have measured the absolute apparent cross section (σ_{app}) for NO₂ photodetachment to an accuracy of $\approx 40\%$ in the region (2.0–2.7) eV. The use of a pulsed, tunable dye laser has permitted observation of cross sections as small as $2 \times 10^{-20} \text{ cm}^2$. Through simulation of the observed spectrum, the electron affinity of nitrogen dioxide has been determined to be $(2.36 \pm 0.10) \text{ eV}$. In addition, we have measured σ_{app} for a second ion with $m/e = 46$, labelled NO₂⁺, in the region (1.8–2.2) eV. The most reasonable explanation of this second spectrum is that it is caused by photodetachment of a peroxy isomer of NO₂.

Note added in proof: In an article to be published in J. Am. Chem. Soc., P. Pearson *et al.* calculate that a peroxy isomer of NO₂ exists and that there is a high potential barrier which inhibits conversion of [N–O–O]⁺ to the more stable isomer. This calculation reinforces our conclusion that the two distinct photodetachment spectra observed are caused by [N–O–O]⁺ and [O–N–O]⁺, respectively.

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†Alfred P. Sloan Foundation Fellow, 1972–74.

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¹⁰The dependence of σ_{ij} on $|I_{ij}|^2$ can be demonstrated if it is assumed that the product wavefunction $\psi(\text{NO}_2)e$ adequately represents the state [²A₁NO₂ + e]. This assumption is of general validity except in the immediate vicinity of threshold.

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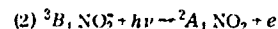
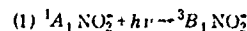
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²⁰The possibility that a fraction of the observed NO₂ photodetachment spectrum is due to the 2-photon process:



is nil because the oscillator strength for (1) is 8×10^{-8} (see Ref. 19).

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